

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 804 492 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

21.07.1999 Bulletin 1999/29

(21) Application number: **95943122.2**

(22) Date of filing: **15.12.1995**

(51) Int Cl.⁶: **C08F 14/26**

(86) International application number:
PCT/US95/16323

(87) International publication number:
WO 96/22313 (25.07.1996 Gazette 1996/34)

(54) **MICROEMULSION POLYMERIZATION SYSTEMS FOR TETRAFLUOROETHYLENE**

MICROEMULSIONSPOLYMERISATION-SYSTEME FÜR TETRAFLUORETHYLEN

SYSTEMES POUR LA POLYMERISATION EN MICROEMULSION DE TETRAFLUOROETHYLENE

(84) Designated Contracting States:
DE FR GB IT SE

(30) Priority: **18.01.1995 US 374010**

(43) Date of publication of application:
05.11.1997 Bulletin 1997/45

(73) Proprietor: **W.L. GORE & ASSOCIATES, INC.**
Newark, Delaware 19714-9206 (US)

(72) Inventors:
• **WU, Huey, Shen**
Newark, DE 19711 (US)

- **HEGENBARTH, Jack**
Wilmington, DE 19803 (US)
- **XIN-KANG, Chen**
Shanghai 200052 (CN)
- **JIAN-GUO, Chen**
Shanghai 200241 (CN)

(74) Representative: **Kador & Partner**
Corneliusstrasse 15
80469 München (DE)

(56) References cited:
EP-A- 0 248 446 **EP-A- 0 612 770**

EP 0 804 492 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

FIELD OF THE INVENTION

[0001] This invention relates to polytetrafluoroethylene of very small particle size and to a process for polymerizing tetrafluoroethylene.

BACKGROUND OF THE INVENTION

[0002] Microemulsions are stable isotropic mixtures of oil, water, and surfactant which form spontaneously upon contact of the ingredients. Other components, such as salt or co-surfactant (such as an alcohol, amine, or other amphiphilic molecule) may also be part of the microemulsion formulation. The oil and water reside in distinct domains separated by an interfacial layer rich in surfactant. Because the domains of oil or water are so small, microemulsions appear visually transparent or translucent. Unlike emulsions, microemulsions are equilibrium phases.

[0003] Microemulsions can have several microstructures, depending upon composition and sometimes temperature and pressure. There are three most common structures. One is an oil-in-water microemulsion in which oil is contained inside distinct domains in a continuous water-rich domain. The second is a water-in-oil microemulsion, in which water is contained inside distinct domains (droplets) in a continuous oil-rich domain. The third is a bicontinuous microemulsions in which there are sample-spanning intertwined paths of both oil and water, separated from each other by the surfactant-rich film.

[0004] Polymerization of emulsified and microemulsified unsaturated hydrocarbon monomers is known, where high reaction rates, high conversions and high molecular weights can be achieved. A microemulsion can be distinguished from a conventional emulsion by its optical clarity, low viscosity, small domain size, thermodynamic stability, and spontaneous formation. Polymerization of microemulsified monomers has many advantages over traditional emulsion polymerization. Microemulsions are normally transparent to translucent so that they are particularly suitable for photochemical reactions, while emulsions are turbid and opaque. Also, the structural diversity of microemulsions (droplets and bicontinuous) is set by thermodynamics, and rapid polymerization may be able to capture some of the original structure. In addition, microemulsion polymerization enables production of stable, monodisperse microlatexes containing colloidal particles smaller than those produced from classical emulsion polymerization processes. Smaller particle size improves the ability to form coatings without microcracking. The increased surface area improves particle fusion during molding operations.

[0005] Emulsion polymerization, as opposed to microemulsion polymerization, of dissolved gaseous

tetrafluoroethylene (PTFE) or its copolymers is a known process. Aqueous colloidal dispersions of PTFE or its copolymers can be prepared in a pressure reactor by placing the gaseous monomer, or a mixture of monomers in contact with an aqueous solution containing at least one surfactant which generally is a fluorinated surfactant, possibly a buffer for keeping the medium at a given pH, and an initiator which is capable of forming free radicals at the polymerization temperature. The free radical initiators can be water soluble peroxides, or alkaline or ammonium persulfates. Persulfate can be used alone if the polymerization temperature is above approximately 50°C, or in association with a reducing agent such as ferrous salt, silver nitrate, or sodium bisulfate if the polymerization temperature is approximately between 5 to 55°C, as described in the U.S. Patent No. 4,384,092.

[0006] The gaseous monomer molecules in the foregoing process enter the aqueous liquid and react to form polymer without first forming a distinct liquid phase. Thus the polymer particles are large particles suspended in the aqueous mixture; and the process is not a true liquid-in-liquid emulsion polymerization. The process is sometimes referred to as dispersion polymerization.

[0007] Additives have been used in attempts to alter the polymerization processes and products thereof. For example, in U.S. Patent 3,721,638, a perfluorinated ether ketone is taught as being added to an aqueous phase polymerization system for polymerizing tetrafluoroethylene, but the initial product is in the form of an aqueous gel.

[0008] Attempts have been made to prepare tetrafluoroethylene copolymers in aqueous dispersion systems. For example, EP 0612770 teaches the copolymerization of TFE and fluoroalkyl perfluorovinyl ethers in an aqueous system containing methylene chloride to obtain dispersion copolymer particles of an average of less than 50 nm in size. One of the surfactants used in the process is perfluorinated octanoic salt.

[0009] U.S. Patent No. 4,864,006 describes the polymerization of TFE and hexafluoropropylene (HFP) to make a copolymer in an aqueous microemulsion containing a perfluoropolyether in which the resulting copolymer particles have a size ranging from 0.041 to 0.070 micrometer.

[0010] Microemulsion polymerization operates by a different mechanism than emulsion polymerization. It involves polymerization of liquid monomer rather than gaseous monomers. Because the polymerization involves polymerizates of unusually small cells of liquid monomer, the resulting polymer particles are unusually small. However, polymerization of liquid TFE is not usually practiced, because of the potential hazards of handling liquid TFE.

[0011] It is desirable to provide a process for polymerizing TFE to produce homopolymer dispersions in which the particle size of the polymer particles is very small. Microemulsion polymerization systems would be

useful in reaching this goal if a means could be found for adapting gaseous TFE to polymerization in an aqueous microemulsion system. Such a TFE polymerization system would result in small particles.

SUMMARY OF THE INVENTION

[0012] The aqueous microemulsion polymerization procedure of the invention involves:

a) forming an aqueous microemulsion of at least one liquid perfluorinated saturated aliphatic or aromatic hydrocarbon or at least one perfluorinated saturated aliphatic or aromatic hydrocarbon that contains one or two oxygen, sulfur or nitrogen atoms, wherein 0.1-40 weight percent of the perfluorinated hydrocarbon and 0.1-40 weight percent of a fluorinated surfactant having the structure $R_fE X$, where R_f is a fluorinated alkyl group with a carbon number between 4 and 16, E is an alkylene group with a carbon number between 0 and 4, and X is an anionic salt such as $COOM$, SO_3M , SO_3NR_2 , SO_4M , a cationic moiety such as quarternary ammonium salt, or an amphoteric moiety such as amino oxide, or a non-ionic moiety such as $(CH_2CH_2O)_nH$; and M is H, Li, Na, K, or NH_4 ; R is a 1 to 5C alkyl group and n is a cardinal number of 2 to 40, are used,

b) feeding gaseous tetrafluoroethylene to the microemulsion; and

c) initiating polymerization by adding a free-radical initiator to the mixture of step b) at a temperature between 0 and 150°C.

[0013] Very small aqueous dispersion polytetrafluoroethylene particles are formed as a result of the polymerization, an average particle size of on the order of 80 nm or less (0.08 micrometer). The average particle size may be less than 60nm or even less than 30 nm.

DETAILED DESCRIPTION OF THE INVENTION

[0014] In this invention, an aqueous microemulsion polymerization procedure is described for producing unusually small particles of polytetrafluoroethylene (PTFE), in which the polymerization of TFE gas is carried out in the presence of microemulsified seed particles or micelles of a liquid perfluorinated hydrocarbon that is a saturated aliphatic or aromatic organic compound having up to 2 oxygen, nitrogen, or sulfur atoms and a molecular weight preferably below 500.

[0015] The polymer particles so produced are usually small, being on the order of an average size of 1 to 80 nanometers (0.001 to 0.080 micrometer), preferably 1 to 60 nanometers and most preferably 1 to 30 nanometers. It is believed that such unusually small polymer

particles are obtained because polymerization of the gaseous TFE takes place inside the very small micelles of the hydrocarbon organic compound in the microemulsion.

[0016] The perfluorinated hydrocarbon is a low molecular weight compound that is liquid at the temperature at which polymerization is carried out. The molecular weight is preferably less than 500. The perfluorinated hydrocarbon preferably has a boiling point less than 230°C. The perfluorinated hydrocarbon can be a perfluorinated saturated aliphatic compound such as a perfluorinated alkane; a perfluorinated aromatic compound such as perfluorinated benzene, or perfluorinated tetradecahydro phenanthrene. It can also be a perfluorinated alkyl amine such as a perfluorinated trialkyl amine. It can also be a perfluorinated cyclic aliphatic, such as decalin; and preferably a heterocyclic aliphatic compound containing oxygen or sulfur in the ring, such as perfluoro-2-butyl tetrahydrofuran.

[0017] Examples of perfluorinated hydrocarbons include perfluoro-2-butyltetrahydrofuran, perfluorodecalin, perfluorodimethyldecalin, perfluoromethylcyclohexane, perfluoro(1,3-dimethylcyclohexane), perfluorodimethyldecahydronaphthalene, perfluorofluorene, perfluoro(tetradecahydronaphthalene), perfluorotetracosane, perfluorokerosenes, octafluoronaphthalene, oligomers of poly(chlorotrifluoroethylene), perfluoro(trialkylamine) such as perfluoro(tripropylamine), perfluoro(tributylamine), or perfluoro(tripentylamine), and octafluorotoluene, hexafluorobenzene, and commercial fluorinated solvents, such as Fluorinert FC-75 produced by 3M. The fluorinated alkanes can be linear or branched, with a carbon atom number between 3 and 20. Oxygen, nitrogen or sulfur atoms can be present in the molecules, but the number of such atoms per molecule should be 2 or less.

[0018] The preparation of the microemulsion depends on careful selection of the ingredients. The microemulsion is prepared by mixing water, perfluorinated hydrocarbon, fluorinated surfactant(s), and optionally cosolvents or inorganic salts. The amounts employed are 0.1-40 weight percent, preferably 0.1-20, of the perfluorinated hydrocarbon, 0.1-40 weight percent, preferably 0.1-25, of the surfactant and optionally cosurfactants; with the remainder water. The microemulsified perfluorinated hydrocarbons are believed to serve as microreactors for fluorinated monomers to enter and to be polymerized. The average particle size of the microemulsions can be in the range of 1 to 80 nanometer, preferably 1 to 60, most preferably 1 to 30. The temperature of the microemulsion formation can be between 0 to 150°C, preferably 40 to 100°C.

[0019] The fluorinated surfactant has the structure $R_fE X$, where R_f is a fluorinated alkyl group with a carbon number between 4 and 16, E is an alkylene group with a carbon number between 0 and 4, and X is an anionic salt such as $COOM$, SO_3M , SO_3NR_2 , SO_4M , a cationic moiety such as quarternary ammonium salt, or an am-

photeric moiety such as aminoxide, or a non-ionic moiety such as $(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$; and M is H, Li, Na, K, or NH_4 ; R is a 1 to 5C alkyl group and n is a cardinal number of 2 to 40.

[0020] When tetrafluoroethylene is referred to herein, it is understood the term includes the so-called modified "homopolymer, in which the polymer chain includes very small amounts of units derived from perfluorol(propyl vinyl ether) or hexafluoropropylene.

[0021] To initiate polymerization, the temperature of the microemulsion is adjusted to between 0 and 150°C, preferably 40 to 100°C. Initiators for polymerization include free-radical initiators, such as persulfates, azo initiators, peroxides, or photo initiators which can generate free radicals by ultraviolet or gamma rays. Amount of initiators present can range between 0.001 to 5 percent by weight based on the final polymer content. Co-solvents such as an alcohol, amines or other amphiphilic molecules, or salt can be employed if desired to facilitate formation of the microemulsion.

[0022] Tetrafluoroethylene is introduced to the reactor from the vapor phase into the aqueous microemulsion phase. Sufficient mixing between liquid and vapor phase is important to encourage mass transfer. The mechanism of forming the ultra small polymer particles is not fully understood. It is believed that the higher the solubility of the tetrafluoroethylene monomer in the perfluorinated hydrocarbon, the better to achieve the original microemulsion particle size and shape. The time of reaction may be between 1 and 500 minutes.

[0023] The resulting polymer particles in the resulting dispersion have an average particle size of between 1 and 80 nanometer, preferably 1 to 60, most preferably 1 to 30, and a polymer average molecular weight of over 100,000, preferably over 1,000,000. The unusually small particle size provides a polymer system with a number of advantages over systems containing larger particles. The system is an aqueous colloidal dispersion, and is clear rather than turbid.

[0024] A small amount of units from comonomers may be present in the polymer, provided the amount of comonomer that can be present is not so great as to change the nature of the product that would be obtained if PTFE had been the product. In other words, the copolymer is still not melt processible. The comonomer can be a halogenated (chlorine or fluorine) olefin of 2-18 carbon atoms, for example vinyl chloride, vinylidene chloride, chlorotrifluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ether, or the like; hydrogenated unsaturated monomers, such as ethylene, propylene, isobutylene, vinyl acetate, acrylates, or the like; crosslinking agents, such as glycidylvinylether, chloroalkyl vinyl ether, allyl-glycidylether, acrylates, methacrylates, or the like.

[0025] The resulting ultra fine colloidal particles can be mixed with other chemicals, polymers, pigments, carbons, or metals to form a composite material such as a polymer alloy, a strain resistant, mold release coating

on articles, or electronic conductors or shieldings, etc. They can be prepared in the form of organosols to impart ultrafine surface coating on substrates, such as fabrics, metals, ceramics, etc. The ultrafine powder of PTFE can also be used to prepare microporous expanded PTFE articles with ultra small pore size. In addition, the PTFE containing colloidal particles can be used as a white pigment or a modifier which improves flame resistance, non-tackiness, water repellency, soil resistance, corrosion resistance, and weather resistance properties on various substrates, porous or nonporous. The polymers can be also used to form a membrane for filtration, microfiltration or ultrafiltration applications.

15 Test Procedures

Particle Size Determination

[0026] A COULTER N4MD particle size analyzer was used. The mean diameter is measured using light scattering method with helium laser at scattering angle of 90 degree. Each aqueous dispersion sample was diluted about 10,000 times with deionized water before measurement.

Melting Temperature

[0027] The melting temperature of a polymer was determined by Differential Scan Calorimetric (DSC) analysis at a heating rate of 10°C/minute under nitrogen purge. If it shows a major endotherm at the peak of a certain temperature, it is reported as the melting temperature of the polymer.

Heat of Crystallization

[0028] Heat of crystallization of a polymer was also determined by DSC at a heating and cooling rate of 10°C/minute from 200°C to 400°C and back to 200°C under nitrogen purge. Heat of crystallization is recorded during the cooling process.

Decomposition Temperature

[0029] Decomposition temperature of a polymer was determined by thermal gravimetric analysis (TGA) on the solid polymer at a heating rate of 20°C/minute in air. It shows a decomposition temperature curve, where the derivative of the curve has a peak at certain temperature. That temperature is reported as the decomposition temperature of the polymer.

Example 1

[0030] In a 2-liter reactor were added 900 grams of deionized water, 25 grams of Fluorinert FC-75 which is obtained from 3M Corp. and contains at least a major component of perfluoro-(2-butyltetrahydrofuran), 25

grams of ammonium perfluorooctanoate (Fluororad FC-143, 3M). The mixture formed a transparent microemulsion phase at room temperature and was stirred at a speed of about 800 rpm. The reactor was then vacuumed and purged with tetrafluoroethylene gas three times to ensure oxygen content in the mixture to be below 30 ppm. Then the temperature of the mixture was raised and maintained at about 82°C. Then the pressure inside the reactor was raised to about 11 kg/cm² with a supply of tetrafluoroethylene gas. 1.0 grams of ammonium persulfate in 50 grams of water was pumped into the reactor to start the reaction. The pressure inside the reactor was maintained at 11 kg/cm² with a constant supply of tetrafluoroethylene. Reaction proceeded for about 60 minutes after ammonium persulfate was charged. Then additional 0.5 gram of ammonium persulfate in 50 gram of water was charged to the reactor. The reaction continued to proceed for another 70 minutes and was stopped.

[0031] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 12% by weight. The average polymer particle size was determined to be about 25 nanometer. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 327°C and heat of crystallization of 16.31 cal/gram. Thermal decomposition temperature of the polymer was determined to be 531°C. These are typical characteristics of polytetrafluoroethylene.

Example 2

[0032] In a 2-liter reactor were added 900 grams of deionized water, 25 grams of perfluorinated decalin (supplied from PCR), and 25 grams of ammonium perfluorooctanoate (Fluororad FC-143, 3M). The mixture formed a transparent microemulsion phase at room temperature and was stirred at a speed of about 800 rpm. The reactor was then vacuumed and purged with tetrafluoroethylene gas three times to ensure oxygen content in the mixture to be below 30 ppm. Then the temperature of the mixture was raised and maintained at about 82°C. Then the pressure inside the reactor was raised to about 11 kg/cm² with a constant supply of tetrafluoroethylene. Reaction proceeded for about 60 minutes after ammonium persulfate was charged. Then additional 1.0 grams of ammonium persulfate in 50 grams of water was charged to the reactor. The reaction continued to proceed for another 100 minutes and was stopped.

[0033] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 14% by weight. The average polymer particle size was determined to be about 20 nanometer. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 325°C and heat of crystallization of 16.35 cal/gram. Thermal decomposition temperature of the polymer was deter-

mined to be 531°C. These are typical characteristics of polytetrafluoroethylene.

Example 3

[0034] In a 2-liter reactor were added 900 grams of deionized water, 50 grams of Fluorinert FC-75 (3M), and 50 grams of ammonium perfluorooctanoate (Fluororad FC-143, 3M). The mixture formed a transparent microemulsion phase at room temperature and was stirred at a speed of about 800 rpm. The reactor was then vacuumed and purged with tetrafluoroethylene gas three times to ensure oxygen content in the mixture to be below 30 ppm. Then the temperature of the mixture was raised and maintained to be about 82°C. Then the pressure inside the reactor was raised to about 11 kg/cm² with a supply of tetrafluoroethylene gas. 1.0 grams of ammonium persulfate in 100 grams of water was pumped into the reactor to start the reaction. The pressure inside the reactor was maintained at 11 kg/cm² with a constant supply of tetrafluoroethylene. Reaction proceeded for about 160 minutes after ammonium persulfate was charged. Then the reaction was stopped.

[0035] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 16% by weight. The average polymer particle size was determined to be about 32 nanometer. Differential Scan Calorimetric (DSC) analysis of the polymer shows the melting temperature peak of 329°C and heat of crystallization of 16.71 cal/gram. Thermal decomposition temperature of the polymer was determined to be 543°C. These are typical characteristics of polytetrafluoroethylene.

Example 4

[0036] In a 2-liter reactor were added 900 grams of deionized water, 25 grams of perfluorinated tetradecahydrophenanthrene (supplied from PCR), and 25 grams of ammonium perfluorooctanoate (Fluororad FC-143, 3M). The mixture formed a transparent microemulsion phase at room temperature and was stirred at a speed of about 800 rpm. The reactor was then vacuumed and purged with tetrafluoroethylene gas three times to ensure oxygen content in the mixture to be below 30 ppm. Then the temperature of the mixture was raised and maintained at about 82°C. Then the pressure inside the reactor was raised to about 11 kg/cm² with a supply of tetrafluoroethylene gas. 1.0 grams of ammonium persulfate in 100 grams of water was pumped into the reactor to start the reaction. The pressure inside the reactor was maintained at 11 kg/cm² with a constant supply of tetrafluoroethylene. Reaction proceeded for about 176 minutes after ammonium persulfate was charged. Then the reaction was stopped.

[0037] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 23% by weight. the average polymer par-

ticle size was determined to be about 41 nanometer. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 328°C and heat of crystallization of 15.78 cal/gram. Thermal decomposition temperature of the polymer was determined to be 554°C. These are typical characteristics of polytetrafluoroethylene.

Example 5

[0038] In a 2-liter reactor were added 900 grams of deionized water, 50 grams of Fluorinert FC-75 (3M), and 100 grams of ammonium perfluorooctanoate (Fluororad FC-143, 3M). The mixture formed a transparent micro-emulsion phase at room temperature and was stirred at a speed of about 800 rpm. The reactor was then vacuumed and purged with tetrafluoroethylene gas three times to ensure oxygen content in the mixture to be below 30 ppm. Then the temperature of the mixture was raised and maintained at about 82°C. Then the pressure inside the reactor was raised to about 11 kg/cm² with a supply of tetrafluoroethylene gas. 1.0 grams of ammonium persulfate in 100 grams of water was pumped into the reactor to start the reaction. The pressure inside the reactor was maintained at 11 kg/cm² with a constant supply of tetrafluoroethylene. Reaction proceeded for about 172 minutes after ammonium persulfate was charged. Then the reaction was stopped.

[0039] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 18% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 327°C and heat of crystallization of 15.43 cal/gram. Thermal decomposition temperature of the polymer was determined to be 527°C. These are typical characteristics of polytetrafluoroethylene.

Example 6

[0040] Example 5 was repeated except that 50 grams of perfluorinated decalin (supplied by PCR) was used instead of 50 grams of Fluorinert FC-75, and the total reaction time after the initiator was added was about 160 minutes.

[0041] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 20% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 328°C and heat of crystallization of 15.60 cal/gram. Thermal decomposition temperature of the polymer was determined to be 535°C. These are typical characteristics of polytetrafluoroethylene.

Example 7

[0042] Example 5 was repeated except that 50 grams of perfluorinated heptane (supplied by PCR) was used

instead of 50 grams of Fluorinert FC-75, and the total reaction time after the initiator was added was about 145 minutes.

[0043] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 16% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 326°C and heat of crystallization of 16.03 cal/gram. Thermal decomposition temperature of the polymer was determined to be 542°C. These are typical characteristics of polytetrafluoroethylene.

Example 8

[0044] Example 5 was repeated except that 50 grams of perfluorinated octane (supplied by PCR) was used instead of 50 grams of Fluorinert FC-75, and the total reaction time after the initiator was added was about 160 minutes.

[0045] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 18% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 328°C and heat of crystallization of 16.33 cal/gram. Thermal decomposition temperature of the polymer was determined to be a peak at 529°C. These are typical characters of polytetrafluoroethylene.

Example 9

[0046] Example 5 was repeated except that 50 grams of hexafluorobenzene (supplied by PCR) was used instead of 50 grams of Fluorinert FC-75, and the total reaction time after the initiator was added was about 178 minutes.

[0047] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 20% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 327°C and heat of crystallization of 12.66 cal/gram. Thermal decomposition temperature of the polymer was determined to be 539°C. These are typical characteristics of polytetrafluoroethylene.

Example 10

[0048] Example 5 was repeated except that 50 grams of perfluorinated triptentylamine (supplied by PCR) was used instead of 50 grams of Fluorinert FC-75, and the total reaction time after the initiator was added was about 180 minutes.

[0049] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 21% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 327°C and heat of crystallization of 14.26 cal/gram. Thermal decomposition temperature of the polymer was determined to be 539°C. These are

typical characteristics of polytetrafluoroethylene.

Example 11

[0050] Example 5 was repeated except that 50 grams of perfluorinated 1,3-dimethyl cyclohexane (supplied by PCR) was used instead of 50 grams of Fluorinert FC-75, and the total reaction time after the initiator was added was about 207 minutes.

[0051] The dispersion produced from the above reaction was clear and transparent. The solid polymer content was about 21% by weight. Differential Scan Calorimetric (DSC) analysis of the polymer showed a melting temperature peak of 328°C and heat of crystallization of 15.28 cal/gram. Thermal decomposition temperature of the polymer was determined to be 531°C. these are typical characteristics of polytetrafluoroethylene.

[0052] The clarity and transparency of the dispersions produced in the Examples is indicative of the smallness, on the order of less than 0.06 micrometer, of the colloidal particles in the dispersion.

Claims

1. Process for preparing an aqueous microemulsion of polymer particles which comprises:

a) forming an aqueous microemulsion of at least one liquid perfluorinated saturated aliphatic or aromatic hydrocarbon or at least one perfluorinated saturated aliphatic or aromatic hydrocarbon that contains one or two oxygen, sulfur or nitrogen atoms, wherein 0.1-40 weight percent of the perfluorinated hydrocarbon and 0.1-40 weight percent of a fluorinated surfactant having the structure $R_fE X$, where R_f is a fluorinated alkyl group with a carbon number between 4 and 16, E is an alkylene group with a carbon number between 0 and 4, and X is an anionic salt such as $COOM$, SO_3M , SO_3NR_2 , SO_4M , a cationic moiety such as quaternary ammonium salt, or an amphoteric moiety such as aminoxide, or a non-ionic moiety such as $(CH_2CH_2O)_nH$; and M is H, Li, Na, K, or NH_4 ; R is a 1 to 5C alkyl group and n is a cardinal number of 2 to 40, are used,

b) feeding gaseous tetrafluoroethylene to the microemulsion; and

c) initiating polymerization by adding a free-radical initiator to the mixture of step b) at a temperature between 0 and 150°C.

2. Process of Claim 1, wherein the liquid perfluorinated saturated aliphatic or aromatic hydrocarbon is selected from the class consisting of a perfluorinated

ed saturated aliphatic compound, a perfluorinated aromatic compound, a perfluorinated alkyl amine, and a perfluorinated saturated cyclic aliphatic compound that can have oxygen, sulfur or nitrogen in the ring.

3. An aqueous microemulsion of polytetrafluoroethylene particles in which the average particle size is between 0.01 and 0.08 micrometer, which microemulsion also contains at least one liquid perfluorinated saturated aliphatic or aromatic hydrocarbon or at least one perfluorinated saturated aliphatic or aromatic hydrocarbon that contains one or two oxygen, sulfur or nitrogen atoms.
4. The aqueous microemulsion of Claim 3 in which the average particle size is between 0.01 and 0.06 micrometer.
5. The aqueous microemulsion of Claim 3 in which the average particle size is between 0.01 and .03 micrometer.
6. An aqueous microemulsion comprising at least one perfluorinated saturated aliphatic or aromatic hydrocarbon that contains up to two oxygen, sulfur, or nitrogen and has a molecular weight less than 500, and a fluorinated organic surfactant.
7. The microemulsion of Claim 6 wherein the hydrocarbon contains 3-20 carbon atoms and containing 1 or 2 oxygen or nitrogen atoms.

Revendications

1. Procédé de préparation d'une microémulsion aqueuse de particules de polymère qui comprend:

a) la formation d'une microémulsion aqueuse d'au moins un hydrocarbure aromatique ou aliphatique saturé, perfluoré, liquide ou d'au moins un hydrocarbure aromatique ou aliphatique saturé, perfluoré qui contient un ou deux atomes d'oxygène, de soufre ou d'azote, dans laquelle on utilise 0,1 à 40 pour-cent en poids de l'hydrocarbure perfluoré et 0,1 à 40 pour-cent en poids d'un dérivé tensio-actif fluoré ayant la structure $R_f E X$, dans laquelle R_f est un groupe alkyle fluoré ayant un nombre d'atomes de carbone compris entre 4 et 16, E représente un groupe alkylène ayant un nombre d'atomes de carbone compris entre 0 et 4 et X est un sel anionique tel que $COOM$, SO_3M , SO_3NR_2 , SO_4M , un fragment cationique tel qu'un sel d'ammonium quaternaire ou un fragment amphotère tel qu'un aminoxyde, ou un fragment non ionique tel que $(CH_2CH_2O)_nH$; et M

représente H, Li, Na, K ou NH_4 ; R est un groupe alkyle en C_{1-5} et n est un nombre cardinal variant de 2 à 40,

b) l'introduction de tétrafluoroéthylène gazeux dans la microémulsion; et

c) l'amorçage de la polymérisation par l'addition d'un amorceur de radicaux libres au mélange de l'étape b) à une température comprise entre 0 et 150°C .

2. Procédé selon la revendication 1, dans lequel l'hydrocarbure aromatique ou aliphatique saturé, perfluoré, liquide est choisi dans le groupe comprenant un composé aliphatique saturé perfluoré, un composé aromatique perfluoré, une alkylamine perfluorée et un composé aliphatique cyclique saturé perfluoré qui peut avoir un atome d'oxygène, de soufre ou d'azote dans le noyau.

3. Microémulsion aqueuse de particules de polytétrafluoroéthylène dans laquelle la grosseur moyenne des particules est comprise entre 0,01 et 0,08 micromètres, laquelle microémulsion contient aussi au moins un hydrocarbure aromatique ou aliphatique saturé, perfluoré, liquide ou au moins un hydrocarbure aromatique ou aliphatique saturé perfluoré qui contient un ou deux atomes d'oxygène, de soufre ou d'azote.

4. Microémulsion aqueuse selon la revendication 3, dans laquelle la grosseur moyenne des particules est comprise entre 0,01 et 0,06 micromètres.

5. Microémulsion aqueuse selon la revendication 3, dans laquelle la grosseur moyenne des particules est comprise entre 0,01 et 0,03 micromètres.

6. Microémulsion aqueuse qui comprend au moins un hydrocarbure aromatique ou aliphatique saturé perfluoré qui contient jusqu'à deux atomes d'oxygène, de soufre ou d'azote et possède une masse moléculaire inférieure à 500, et un dérivé tensio-actif organique fluoré.

7. Microémulsion selon la revendication 6, dans laquelle l'hydrocarbure contient 3 - 20 atomes de carbone et contient 1 ou 2 atomes d'oxygène ou d'azote.

Patentansprüche

1. Verfahren zur Herstellung einer wässrigen Mikroemulsion aus Polymer-partikeln, das das:

a) Bilden einer wässrigen Mikroemulsion wenigstens eines flüssigen perfluorierten gesättigten aliphatischen oder aromatischen Kohlen-

wasserstoffes oder wenigstens eines perfluorierten gesättigten aliphatischen oder aromatischen Kohlenwasserstoffes, der ein oder zwei Sauerstoff-, Schwefel- oder Stickstoffatome enthält, worin 0,1 bis 40 Gewichtsprozent des perfluorierten Kohlenwasserstoffes und 0,1 bis 40 Gewichtsprozent eines fluorierten Tensids, das die Struktur R_fEX hat, wo R_f eine fluorierte Alkylgruppe mit einer Kohlenstoffanzahl zwischen 4 und 16 ist, E eine Alkylengruppe mit einer Kohlenstoffanzahl zwischen 0 und 4 ist und X ein anionisches Salz wie COOM , SO_3M , SO_3NR_2 , SO_4M , eine kationische Komponente wie ein quaternäres Ammoniumsalz oder eine amphotere Komponente wie Aminoxyd oder eine nichtionische Komponente wie $(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ist; und M H, Li, Na, K oder NH_4 ist; R eine 1 bis 5 C-Alkylgruppe und n eine Ganzzahl von 2 bis 40 ist, verwendet werden, b) Einbringen von gasförmigem Tetrafluorethylen in die Mikroemulsion und c) Initiieren der Polymerisation durch Zugabe eines Radikalinitiators zu dem Gemisch von Schritt b) bei einer Temperatur zwischen 0 und 150°C umfaßt.

2. Das Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der flüssige perfluorierter gesättigter aliphatischer oder aromatischer Kohlenwasserstoff aus der Masse ausgewählt wird, die aus einer perfluorierten gesättigten aliphatischen Verbindung, einer perfluorierten aromatischen Verbindung, einem perfluorierten Alkylamin und einer perfluorierten gesättigten cycloaliphatischen Verbindung, die Sauerstoff, Schwefel oder Stickstoff im Ring haben kann, besteht.

3. Eine wässrige Mikroemulsion aus Polytetrafluorethylenpartikeln, in der die mittlere Partikelgröße zwischen 0,01 und 0,08 μm ist, wobei die Mikroemulsion ebenso wenigstens einen flüssigen perfluorierten gesättigten aliphatischen oder aromatischen Kohlenwasserstoff oder wenigstens einen perfluorierten gesättigten aliphatischen oder aromatischen Kohlenwasserstoff enthält, der ein oder zwei Sauerstoff-, Schwefel- oder Stickstoffatome enthält.

4. Die wässrige Mikroemulsion nach Anspruch 3, dadurch gekennzeichnet, daß die mittlere Partikelgröße zwischen 0,01 und 0,06 μm ist.

5. Die wässrige Mikroemulsion nach Anspruch 3, dadurch gekennzeichnet, daß die mittlere Partikelgröße zwischen 0,01 und 0,03 μm ist.

6. Eine wässrige Mikroemulsion, die wenigstens einen perfluorierten gesättigten aliphatischen oder

aromatischen Kohlenwasserstoff, der bis zu zwei Sauerstoff-, Schwefel- oder Stickstoffatome enthält und ein Molekulargewicht von weniger als 500 hat, und ein fluoriertes organisches Tensid umfaßt.

5

7. Die Mikroemulsion nach Anspruch 6, dadurch gekennzeichnet, daß der Kohlenwasserstoff 3 bis 20 Kohlenstoffatome enthält und er 1 oder 2 Sauerstoff- oder Stickstoffatome enthält.

10

15

20

25

30

35

40

45

50

55